

ORGANIC CHEMISTRY

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Brooks/Cole Publishing Company *Monterey, California*

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Printed in the United States of America

10 9 8 7 6

Library of Congress Cataloging in Publication Data

*McMurry, John.
Organic chemistry.*

*(The Brooks/Cole series in chemistry)
Includes index.*

*1. Chemistry, Organic. I. Title. II. Series.
QD251.2.M43 1984 547 83-7744*

ISBN 0-534-01204-3

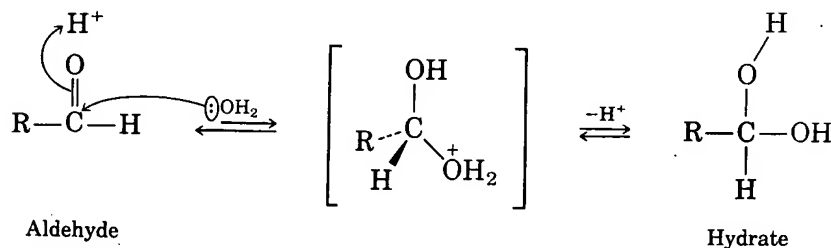
*Sponsoring Editor: Michael Needham
Editorial Assistant: Lorraine McCloud
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Production Coordinator: Joan Marsh
Manuscript Editor: Gloria Joyce
Interior and Cover Design: Stan Rice
Interior Illustration: Vantage Art, Inc.
Typesetting: Jonathan Peck Typographers, Ltd.*

On the Cover: The cover drawings of a molecule recently synthesized at Cornell University were provided by Molecular Design Limited, Hayward, California. They were generated by the MACCS[®] and SPACFIL computer programs for the storage, retrieval, modeling, and display of chemical structures. (Additional airbrush background by Tim Keenan.)

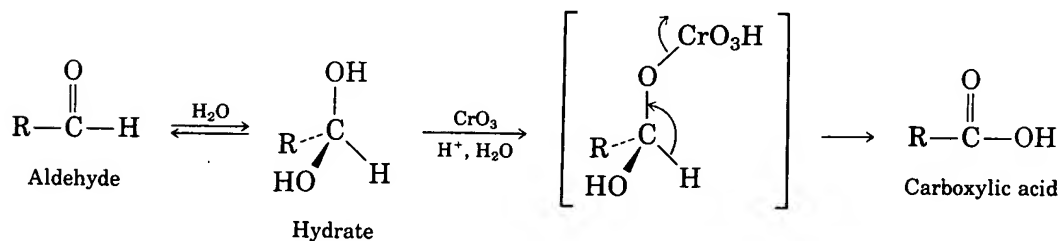
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A shiny mirror of metallic silver is deposited on the walls of the flask during a Tollens oxidation; observation of such a mirror forms the basis of an old qualitative test for the presence of an aldehyde functional group in a molecule of unknown structure. A small sample of the unknown is dissolved in ethanol in a test tube, and a few drops of the Tollens reagent are added. If the test tube becomes silvery, the unknown is presumed to be an aldehyde.

Aldehyde oxidations are thought to occur through intermediate 1,1-diols or hydrates, which are formed by nucleophilic addition of water to the carbonyl group. Hydrate formation is reversible—the hydrate can eliminate water to re-form aldehyde—and the equilibrium position of the reaction usually favors the aldehyde:



Once formed, and even though present in small amounts, the hydrate reacts like any normal primary or secondary alcohol and is oxidized to a carbonyl compound (Section 20.10).



Ketones are inert to most common oxidizing agents but undergo a slow cleavage reaction when treated with hot alkaline KMnO_4 . The carbon-carbon bond next to the carbonyl group is broken and carboxylic acid fragments are produced. The reaction is only useful for symmetrical ketones such as cyclohexanone, however, since product mixtures are formed from unsymmetrical ketones.

